Wet Process Technology Research At Eastern Regional Research Center

During the past two years the Wet Processing Technology group at ERRC has been analyzing the complex chemical and physical changes which take place as a raw hide is processed through to the blue. The project has a wide scope requiring a variety of disciplines and when the initial phases are completed a powerful tool will be available to help achieve the longer range goals of modifying the tanning process for the benefit of the tanner, the consumer, and the environment. This will require a thorough understanding of the chemical and physical changes occurring in modern manufacturing processes and the ability to carry out these processes on a pilot scale in the experimental tannery.

When the project was initiated, several short-range goals were established. The first was to be able to convert raw hides to the blue on site, the second was to develop accurate and reproducible procedures for sampling and analyzing both the hide and the process solution immediately after each stage. Another goal was to manage the enormous quantity of data which would be generated. The final goal was the development of a standard process which will be used as the baseline against which future experiments on modified procedures will be measured. Each of these goals has been partially achieved.

Survey of the Industry

Many papers have been published which describe the chemical analyses and physical testing on blue stock produced from a variety of tanning processes. However, most of this past work was done on processes which are not typical of the rapid methods which are being used today.

The first task in this project was to obtain actual modern procedures. The proposed project was discussed with members of the tanning industry and as a result, nine tanneries agreed to complete a rather extensive and detailed survey on how they process hides through to the blue. Without their cooperation this work could never have gotten off the ground. The survey was all encompassing. For example typical data requested included: equipment used, raw material, process data, float temperature, pH, concentration of chemicals, as well as time of process, labor, space, and disposition of floats. Other processing steps required details on effluent treatment. The survey included questions on storage and movement of the hides through the beamhouse, from sorting and siding, through wringing, splitting, and shaving. The information concerning labor, equipment, and space was used as input to a computer model of the tanning process. This model was developed at Oklahoma State University. The chemical and physical properties data that are being accumulated ultimately will also be fed into this model.

This paper was prepared by M.M. Taylor, E.J. Diefendorf, M.V. Hannigan, D.G. Bailey and S.H. Fearheller of the Eastern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, and was delivered at the Annual Meeting of the American Leather Chemists Association held in June 1981 at Hilton Head, S.C.

TABLE 1
CHEMICAL ANALYSES
HIDE SAMPLES

Moisture	Total Kjeldahl nitrogren
Dry substance	Oil and grease
Ash	Calcium
Volatile solids	Chloride
Chromic oxide	

TABLE 2
CHEMICAL ANALYSES
EFFLUENT SAMPLES

Dissolved solids	COD
Total Kjeldahl nitrogen	Density
Oil and grease	pH
Calcium	Alkalinity
Chloride	Sulphide
Chromic Oxide	Ammonia
Total solids, ash, volatiles	
Suspended solids, ash, volatiles	

Because of the detail of the survey, we were able to set up pilot scale runs for each of the nine different tanning processes. Several of these industrial processes have already been changed, but all at one time were used to produce commercial leather. No one can call the United States tanning industry static.

Pilot Scale Runs

In all, a total of 18 batches have been run and, in each batch, four to six sides were processed. An attempt was made to duplicate these industrial systems as closely as possible. All conditions—time, temperature, amounts of chemicals, floats, washes, and pH—were repeated with as much accuracy as possible. To monitor changes taking place in a process, it was extremely important that sampling of the hide and the floats was representative of the whole. It was important that weights of hides, chemicals, and liquids at the start of a stage were carefully measured and recorded. For example, after a processing stage was complete, the floats as well as washes were pumped from the vessel and collected in an appropriate container and weighed. The solutions were stirred vigorously before a representative sample for analysis was taken. Next the hides were removed from the vessel and weighed. Four inch squares from four sides were taken for chemical analysis, 8″ × 11″ samples were analysis, 8" × 11" samples were taken from matched sides for physical testing, and 1" square samples from matched sides were taken for microscopic examination. Sample weights were subtracted from the hide weight, recorded, and adjustments were then made for calculation of the weight of chemicals to be added to the next step. The hides were returned to the vessel and the next processing stage was begun.

Tables 1 and 2 indicate the range of chemical analyses which were run on the hide and process solutions. Physical test data included tensile strength, stitch tear, and ball burst. Almost all of the chemical analysees performed were by ALCA standard methods, although sometimes slight modifications were used due to the nature of the sample. Calcium and chromium analyses were done by atomic absorption. Almost all analyses were run in triplicate. The physical testing was carried out in triplicate for tensile and single tests for ball burst and stitch tear. Precision improved from the initial runs due to the development and refinement of techniques appropriate to the samples. We felt that the development of a sophisticated system of sampling and analysis was in itself a major accomplishment of this project.

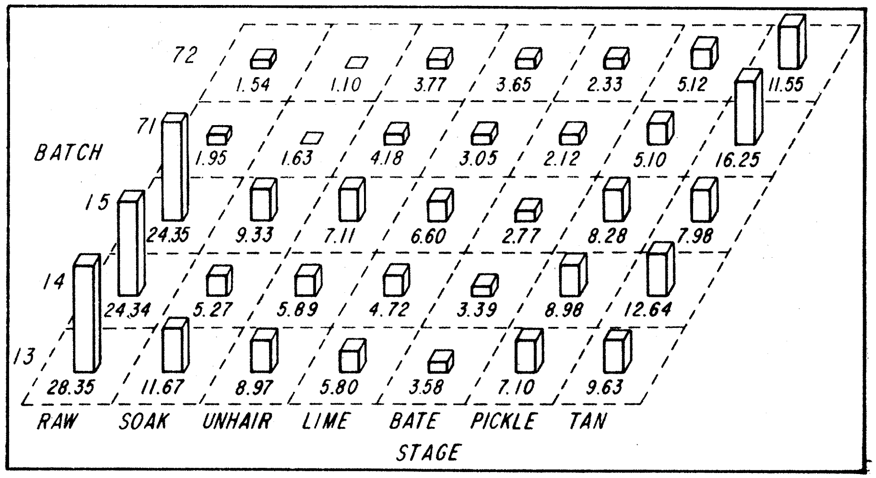

Figure 1. Percent ash (MFB) in hide by batch and stage.

Data Handling

Seven to nine hundred pieces of data were collected from each batch. Data handling itself was difficult, but an essential part of this work. The following figures show some of the results which have been obtained with the assistance of a computer. Several analyses of the hide as it moves through a process are illustrated, and one can compare processes with each other. The computer has rather conveniently shown these changes in two distinct ways, by three-dimensional graphs and by bar graphs. These are only examples of several analyses which have been done for each run.

Figure 1 is a three-dimensional

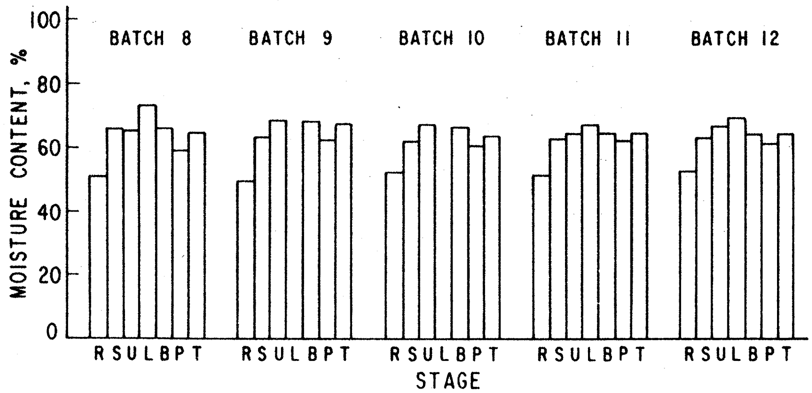

Figure 2. Computer illustration of percent moisture in hide at various stages.

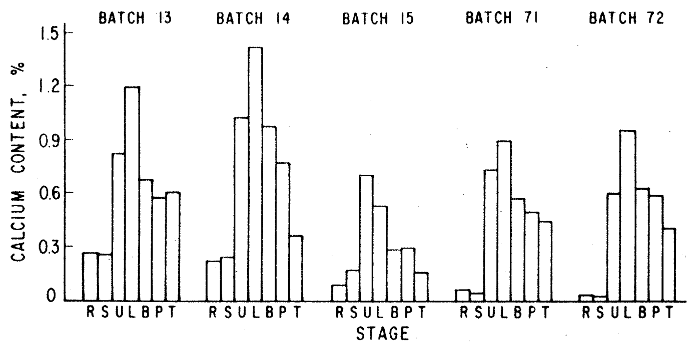

Figure 3. Computer illustration of percent calcium (MFB) in hide at various stages.

graph which represents the percent of ash on a moisture free basis (MFG) in a hide as it is processed from raw to tan. Batches 13, 14 and 15 are brined hides. Batches 71 and 72 are fresh hides. The ash content in raw and soak samples from 71 and 72 are quite low reflecting the absence of salt.

The moisture content of the hide as it goes through the processing stages from five different batches is compared in Figure 2 in a bar graph. The water content in the raw hide varies with the cure of the hides and conditions of storage. However, the moisture content becomes quite uniform as the hide proceeds through processing. In almost all instances, the limed hide has the highest moisture. Batches 9 and 10 illustrate a process where the lime step was combined with unhairing. Hides were not removed from the vessel so no samples were taken for analysis.

Figure 3 illustrates the calcium found in the hide as it moves through each stage from raw to tan. The calcium contents in the raw and soak stages in batches 13 and 14 suggest hard water was used in the cure. Batches 71 and 72 are fresh hides and the calcium content is very low. The highest calcium content in the hide is found after reliming. However, in run 15 this is not the case. This particular process uses an extensive series of washes after the lime and this explains the apparent anomaly. In a process not shown, an increase in calcium in the tanned hide was observed. This was because dolomite lime was used in the neutralization step. The sensitivity of these data from the analyses to the different process variations gives confidence in the analytical procedures that are being used.

To understand the chemical changes it is important to know not only where the specific chemicals are located (in the hide or in the effluent) but also whether an accounting is being made for all of the chemicals used. This materials balance is most important.

A materials balance has been calculated on each batch. An example of a balance is shown in Table 3.

TABLE 3
MATERIALS BALANCE

	% Recovery			
Stage	Solids	Moisture	Ash	Volatile solids
Soak	106	93	98	109
Unhair	107	95	100	109
Lime	99	101	108	97
Bate	96	100	137	94
Pickle	93	99	94	93
Tan	99	90	84	103
Overall recovery	102	96	97	105

This balance reflects moisture, total solids, ash, and volatile solids. It shows the percent recovery for each stage as well as the overall balance. The recoveries are generally quite good. Material balances have also been similarly calculated for chromium showing a 95 to 106 percent recovery and for calcium showing a 93 to 104 percent recovery.

Determining material balances is of course made much easier using a computer. However, the maximum strength of the computer lies in the statistical evaluation of the data. The next level of data analysis, which has just begun, is to find the significant correlations between process steps and the results of the chemical analysis and physical tests. An analysis of variance between each process step and each of the chemical properties will be made.

The results obtained from physical testing of the hide after each processing stage have been analyzed by the computer. In each batch, tensile, elongation, ball burst, and stitch tear have been run on matched side samples. Figure 4 illustrates with use of a three-dimensional graph the trend in extension as the hide moves through the process. The hide reaches the highest extension in the lime and from there is gradually falls off to the blue.

Microscopic Examination

An extensive histological analysis on the hide as it goes through each stage was done. Detailed photomicrographs of selections from each

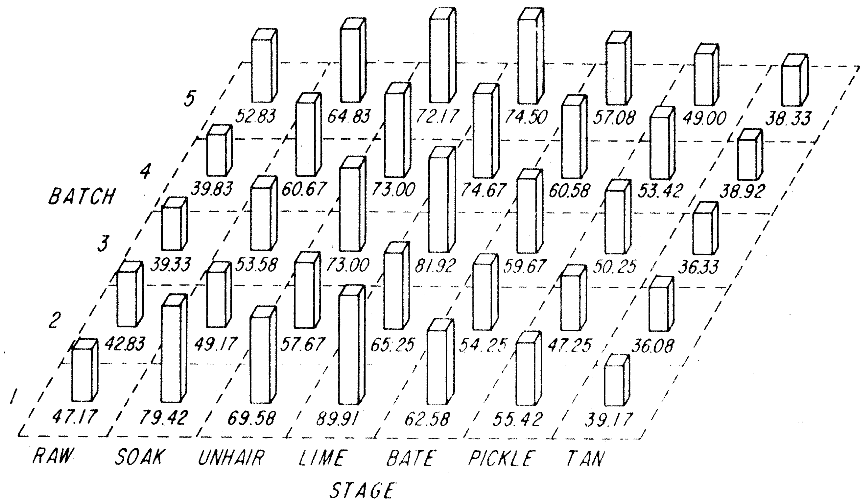

Figure 4. Percent extension by batch and stage.

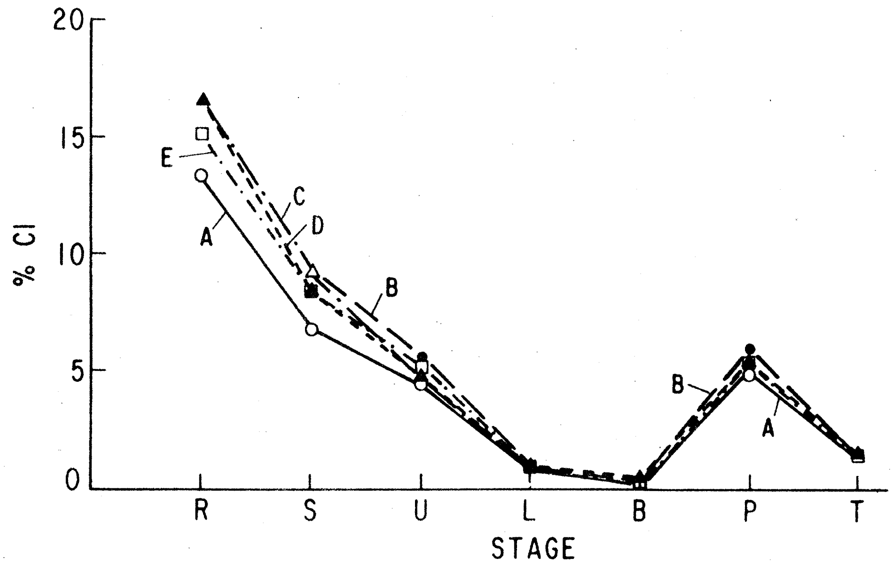

Figure 5. Percent chloride (MFB) in hide.

TABLE 4
HISTOLOGICAL EVALUATION OF SIDES DURING PROCESS

	Numerical rating†		
Batch	Soak	Lime	Blue
3* + 8**	3	4.5	5
4 + 5**	4	4	5
6***	5	5	5
9 + 10**	3	4	5
11** + 14*	3.5	4	4.5
12**	2	2.5	2.5
13*	3	4	5
15*	3.5	5	5

† Rating 1 is poor, 5 is very good.
* Brine cured hides.
** Salt cured hides.
*** Fresh hides was used as a criterion for process effect.

stage were examined. Soaks were evaluated for rehydration of fibers and relaxation of hair roots. Lime stages were evaluated for rehydration of fibers and relaxation of hair roots. Lime stages were evaluated for hair removal, plumping, and the opening up of fiber structure and splitting of fibers. Chrome tanning was evaluated for penetration of chrome. Ash patterns were made showing chrome penetration and salt deposits within the hide. In all these analyses comparisons were not made of variations on a treatment process such as varying length of soaking or the amount of chrome added. Keep in mind these are current commercial processes which already make good, salable leather. As such a similar pattern is seen in each batch examined and that was what was anticipated. As one proceeds from soak to blue, fiber structure is opened, as expected. Table 4 shows a numerical rating of fiber structure for the batches examined.

Critical Questions

After establishing the analytical procedures and the means to handle the data, there still remained two critical questions. To be confident that our pilot plant could reproduce industrial scale processes, we had to establish that individual runs were reproducible and that the blue we produced from the process was comparable to the blue from full scale production. The material balances show the process chemicals are being accounted for, and in fact, the composition of the total effluent as calculated compares well to the data published elsewhere on effluent composition.

Duplication of pilot scale industrial runs has been achieved. Figures 5 and 6 show some of the data from a single process which has been run five times. A tabulation of percent chloride on MFB found in the hide at each processing stage is shown in Figure 5. Batch A was from a lot of salt packed hides and B, C, D, and E were brine cured hides. This could account for the observed initial differences in the raw and soak. Results after the soak are quite close and again suggest good reproducibility.

In Figure 6 data from the analysis of effluent for total Kjeldahl nitrogen, in terms of lbs/1000 of hides, show a similar reproducibility. Variations in unhairing and lime could be expected due to variable amounts of hair on the animal. After this stage the values become very close.

In answer to the comparability of the blue with the corresponding industrial processing, each of the processes for which the chemical and physical analyses had been done were run again without sampling. These sides were then sent to the respective tanners for finishing and evaluation. Five processes were run in this way and all were found acceptable.

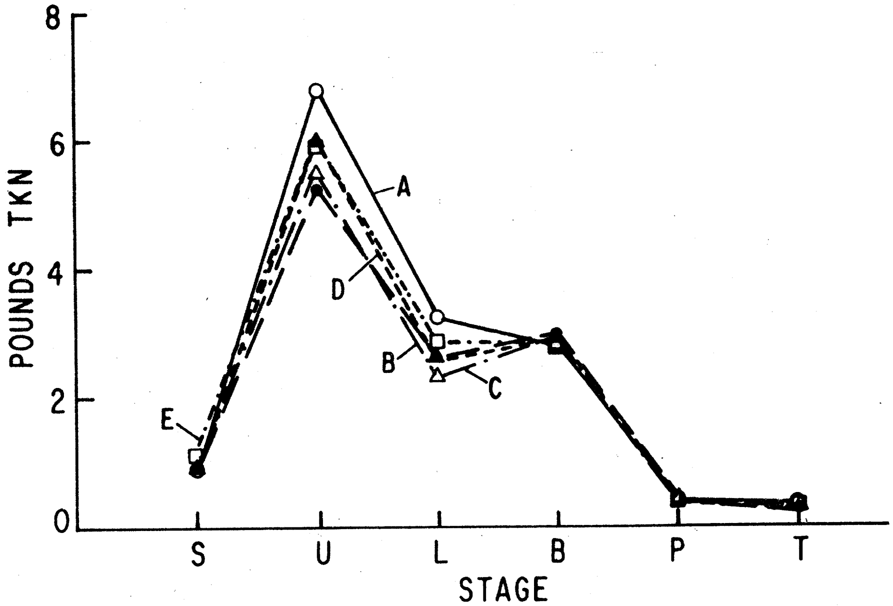

Figure 6. Pounds of TKN/1,000 pounds of hides, found in effluent.

Standard Process

Based on the information gathered so far and the experience gained to date, a standard process has been developed to take hides through to the blue in our pilot plant. This will be referred to as the USDA process and may be the most important product of this project to date. This process will be used as the baseline against which future experiments on modified procedures will be measured. Full chemical, physical, and histological studies have been done on a series of repeat runs using this process. These runs have been completed, and the baseline data with which to compare innovative experimental runs has been determined.

The Future

The next stage of the work will be the close examination of new processes. We would like to emphasize that there is still time for members of the industry to suggest innovative processes to be examined.

This phase of the work is about to begin and in a short time we will report on process modifications based on this work. To achieve what we have done so far has required a great deal of dedication and hard work by our co-workers at ERRC, and we would like to acknowledge those efforts at this time.